05 Environmental Chemistry & Purification, Qualitative, Quantitative Analysis

Environmental Chemistry

Environmental Pollution

Environmental pollution is the effect of undesirable changes in our surroundings that have harmful effects on plants, animals and human beings.

Pollutant

- A substance, which causes pollution, is known as pollutant.
- Pollutants can be solid, liquid or gaseous substances present in greater concentration than in natural abundance and are produced due to human activities or due to natural happenings.

Biodegradable

Pollutant can be degradable like discarded vegetables which rapidly breakdown by natural processes.

Ex. Paper bags and Vegetable waste.

Non-Biodegradable

Pollutant which are slowly degradable, remain in the environment in an unchanged form for many decades.

Ex. Glass waste, e- waste, Metal waste and Plastic waste.

Atmospheric Pollution

- The lowest region of atmosphere in which the human beings along with other organisms live is called troposphere. It extends up to the height of ~10 km from sea level.
- Above the troposphere, between 10 and 50 km above sea level lies stratosphere. The stratosphere contains dinitrogen, dioxygen, ozone and little water vapour.
- The presence of ozone in the stratosphere prevents about 99.5 per cent of the sun's harmful ultraviolet (UV) radiations from reaching the earth's surface.

1. Tropospheric Pollution

Tropospheric pollution occurs due to the presence of undesirable solid or gaseous particles in the air.

(i) Gaseous Air Pollutants

(A) Oxides of Sulphur

Oxides of Sulphur are produced when Sulphur containing fossil fuel is burnt.

- Uncatalysed oxidation of Sulphur dioxide is slow. However, the presence of particulate matter in polluted air catalyses the oxidation of Sulphur dioxide to sulphur trioxide.

$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$

- The reaction can also be promoted by ozone and hydrogen peroxide.

$SO_2(g) + O_3(g) \longrightarrow SO_3(g) + O_2(g)$

$SO_2(g) + H_2O_2(l) \longrightarrow H_2SO_4(aq)$

Adverse effect of Sulphur dioxide

- Sulphur dioxide is a gas that is poisonous to both animals and plants.
- It causes respiratory diseases in human beings.
  (i) Asthma (ii) Bronchitis (iii) Emphysema
- Sulphur dioxide causes irritation to the eyes, resulting in tears and redness.
- High concentration of SO_2 leads to stiffness of flower buds which eventually fall off from plants.

(B) Oxides of Nitrogen

Dinitrogen and dioxygen do not react with each other at a normal temperature. At high altitudes when lightning strikes, they combine to form oxides of nitrogen.

- NO_2 is oxidised to nitrate ion, NO_3^- which is washed into soil, where it serves as a fertilizer.
- In an automobile engine (at high temperature), when fossil fuel is burnt, dinitrogen and dioxygen combine to yield significant quantities of nitric oxide (NO) and nitrogen dioxide (NO_2) as given below:

$$N_2(g) + O_2(g) \xrightarrow{1483\,k} 2NO(g)$$

- No instant reaction with oxygen to give NO_2

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

- Rate of production of NO_2 is faster when nitric oxide reacts with ozone in the stratosphere.

$$NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g)$$

Adverse effect of NO_2

- Respiratory diseases in children.
- The irritant red haze in the traffic and congested places is due to oxides of nitrogen.
- Higher concentrations of NO_2 damage the leaves of plants and retard the rate of photosynthesis.
- It is also a lung irritant.

(C) Hydrocarbons

Hydrocarbons are composed of hydrogen and carbon only and are formed by incomplete combustion of fuel used in automobiles.

Adverse effect of Hydrocarbon

- Hydrocarbons are carcinogenic i.e., they cause cancer.
- Shedding of leaves

(D) Oxide of Carbon

(a) Carbon monoxide

Carbon monoxide (CO) is one of the most serious air pollutants. It is a colourless and odourless gas, highly poisonous to living being because of its ability to block the delivery of oxygen to the organs and tissues.

- Carbon monoxide is produced as a result of incomplete combustion of carbon and carbon containing products like Coal, Petrol, Firewood etc.
- Carbon monoxide is mainly released into the air by automobile exhaust.

Adverse effect of Carbon monoxide

- It blocks the delivery of oxygen to the organs and tissues.
- It binds to haemoglobin to form carboxyhaemoglobin, which is about 300 times more stable than the oxygen-haemoglobin complex. In blood, when the concentration of carboxyhaemoglobin reaches about 3 – 4 per cent, the oxygen carrying capacity of blood is greatly reduced.

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Effect of Oxygen deficiency

- Headache
- Weak eyesight
- Cardiovascular disorders

(b) Carbon dioxide

Carbon dioxide gas is confined to troposphere only. Normally it forms about 0.03 percent by volume of the atmosphere.

- Carbon dioxide (CO_2) is released into the atmosphere by
- Respiration
- Burning of fossil fuels for energy
- Decomposition of lime stone during the manufacturing of Cement.

  $CaCO_3$ (s) $\longrightarrow$ CaO (s) + CO_2 (g)

  (Lime stone)
- Volcanic eruption

BEGINNER'S BOX-1

1. Domestic waste will lead to -

(1) Biodegradable pollution (2) Nondegradable pollution

(3) Thermal pollution of soil (4) Air pollution

2. The major source of BOD in the river Ganga is

(1) Leaf litter (2) Fishes (3) Human waste (4) Aquatic plants

3. If a lake is contaminated with DDT, its highest concentration would be found in

(1) Primary consumer (2) Secondary consumer

(3) Tertiary consumer (4) None of these

4. The most harmful air pollutant produced by automobiles is

(1) HNO_2 (2) NO (3) SO_2 (4) CO

5. Sewage water can be purified by

(1) Aquatic plant (2) Micro organism (3) Penicillin (4) Fishes

Global Warming

- About 75 % of the solar energy reaching the earth is absorbed by the earth's surface, which increases its temperature.
- The rest of the heat radiates back to the atmosphere.
- Some of the heat is trapped by gases such as carbon dioxide, methane, ozone, chlorofluorocarbon compounds (CFCs) and water vapour in the atmosphere. Thus, they add to the heating of the atmosphere. This causes global warming.

Greenhouse Effect

The atmosphere has kept the temperature on earth constant. As the glass in a greenhouse holds the sun's warmth inside, atmosphere traps the sun's heat near the earth's surface and keeps it warm. This is called natural greenhouse effect.

- Factors responsible for Global Warming
- Dichlorodiphenyltrichloroethane (DDT)
- Vehicles

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- Deforestation
- Burning of non-biodegradable waste

Acid Rain

- Normally rain water has a pH of 5.6 due to the presence of H^+ ions formed by the reaction of rain water with carbon dioxide present in the atmosphere.

  $H_2O\ (l) + CO_2\ (g) \rightleftharpoons H_2CO_3(aq)$

  $H_2CO_3\ (aq) \rightleftharpoons H^+\ (aq) + HCO_3^-\ (aq)$

  When the pH of the rain water drops below 5.6, it is called acid rain.
- Burning of fossil fuels (which contain Sulphur and nitrogenous matter) such as coal and oil in power stations and furnaces or petrol and diesel in motor engines produce Sulphur dioxide and nitrogen oxides. SO_2 and NO_2 after oxidation and reaction with water are major contributors to acid rain.

  $2SO_2\ (g) + O_2\ (g) + 2H_2O\ (l) \longrightarrow 2H_2SO_4\ (aq)$

  $4NO_2\ (g) + O_2\ (g) + 2H_2O\ (l) \longrightarrow 4HNO_3\ (aq)$

Adverse effect of Acid Rain

- Acid Rain is harmful for agriculture, trees and plants as it dissolves and washes away nutrients needed for their growth.
- Yellowing of plant leaves is also because of acid rain.
- Weathering of stone buildings
- The Taj Mahal in India has been affected by acid rain.
- Corrosion of metallic structures
- Killing of aquatic life form

(ii) Particulate Pollutants

Particulate pollutants are the minute solid particles present in vehicle emissions, smoke particles from fires, dust particles and ash from industries.

(A) Viable

The viable particulates e.g. bacteria, fungi, moulds, algae etc., are minute living organisms that are dispersed in the atmosphere. Human beings are allergic to some of the fungi found in air. They can also cause plant diseases.

(B) Non-viable

Non-viable particulates may be classified according to their nature and size as follows :

Smoke, Dust, Mists and Fumes.

(a) Smoke

Smoke particulates consist of solid or mixture of solid and liquid particles formed during combustion of organic matter. Examples are cigarette smoke, smoke form burning of fossil fuel, garbage and dry leaves, oil smoke etc.

(b) Dust

Dust is composed of fine solid particles (over, 1 μm in diameter), produced during crushing, grinding and attribution of solid materials. Sand from sand blasting, saw dust from wood works, pulverized coal, cement and fly ash from factories, dust storms etc., are some typical examples of this type of particulate emission.

(c) Mists

Mists are produced by particles of spray liquids and by condensation of vapours in air. Examples are sulphuric acid mist and herbicides and insecticides that miss their targets and travel through air and form mists.

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(d) Fumes

Fumes are generally obtained by the condensation of vapours during sublimation, distillation, boiling and several other chemical reactions. Generally, organic solvents, metals, and metallic oxides form fume particles.

Lead : major air pollutant

- Lead used to be a major air pollutant emitted by vehicles.
- Leaded petrol used to be the primary source of air-borne lead emission in Indian cities.
- This problem has now been overcome by using unleaded petrol in most of the cities in India.
- Lead interferes with the development and maturation of red blood cells.

Smog

The word smog is derived from smoke and fog. This is the most common example of air pollution that occurs in many cities throughout the world

(i) Classical smog

- Classical smog is a mixture of smoke, fog and sulphur dioxide.
- Chemically it is a reducing mixture and so it is also called as reducing smog.

(ii) Photochemical smog

- The main components of the photochemical smog result from the action of sunlight on unsaturated hydrocarbons and nitrogen oxides produced by automobiles and factories. Photochemical smog has high concentration of oxidising agents and is, therefore, called as oxidising smog.
- Ozone is a toxic gas and both NO_2 and O_3 are strong oxidising agents and can react with the unburnt hydrocarbons in the polluted air to produce chemicals such as formaldehyde, acrolein and peroxyacetyl nitrate (PAN).

$3CH_4 + 2O_3 \longrightarrow 3H_2C{=}O + 3H_2O$

Formaldehyde

$H_2C{=}CHCH{=}O$

Acrolein

CH_3COONO_2 (with $=O$ on the carbonyl carbon)

Peroxyacetyl nitrate [PAN]

Effect of photochemical smog

- Both ozone and PAN act as powerful eye irritants.
- Ozone and nitric oxide irritate the nose and throat.
- High concentration ozone and nitric oxide causes headache, chest pain, dryness of the throat, cough and difficulty in breathing.
- Photochemical smog leads to crackling of rubber and extensive damage to plant life. It also causes corrosion of metals, stones, building materials, rubber and painted surfaces.

How can photochemical smog be controlled :

Catalytic converters

- Catalytic converters are used in the automobiles, which prevent the release of nitrogen oxide and hydrocarbons to the atmosphere.
- Certain plants e.g. Pinus, Juniparus, Quercus, Pyrus and Vitis can metabolise nitrogen oxide and therefore, their plantation could help in the matter.

2. Stratospheric Pollution

The upper stratosphere consists of considerable amount of ozone (O_3), which protects us from the harmful ultraviolet (UV) radiations (λ 255 nm) coming from the sun. These radiations cause skin cancer (melanoma) in humans. Therefore, it is important to maintain the ozone shield.

Formation of Ozone

- Ozone in the stratosphere is a product of UV radiations acting on dioxygen (O_2) molecules. The UV radiations split apart molecular oxygen into free oxygen (O) atoms. These oxygen atoms combine with the molecular oxygen to form ozone.

$$O_2\,(g) \xrightarrow{UV} O(g) + O(g)$$

$$O(g) + O_2\,(g) \rightleftharpoons O_3\,(g)$$

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Chlorofluorocarbon

- Compounds (CFCs), also known as freons.
- These compounds are nonreactive, non-flammable, non-toxic organic molecules.
- Once CFCs are released in the atmosphere, they get broken down by powerful UV radiations, releasing chlorine free radical.

Summer

In summer season, nitrogen dioxide and methane react with chlorine monoxide (reaction i) and chlorine atoms (reaction ii) forming chlorine sinks, preventing much ozone depletion

$Cl\dot{O}\,(g) + NO_2\,(g) \longrightarrow ClONO_2(g)$ (i)

$\dot{C}l(g) + CH4(g) \longrightarrow \dot{C}H_3(g) + HCl(g)$ (ii)

Winter

In winter, special type of clouds called polar stratospheric clouds provide surface on which chlorine nitrate formed (reaction i) gets hydrolysed to form hypochlorous acid (reaction (ii)).

$ClONO_2(g) + H_2O(g) \longrightarrow HOCl(g) + HNO_3(g)$ (i)

$ClONO_2(g) + HCl(g) \longrightarrow Cl_2(g) + HNO_3(g)$ (ii)

Spring

When sunlight returns to the Antarctica in the spring, the sun's warmth breaks up the clouds and HOCl and Cl_2 are photolysed by sunlight, as given in reactions (i) and (ii).

$HOCl\,(g) \xrightarrow{hv} \dot{O}H\,(g) + (\dot{C}l)\,(g)$ (i)

$Cl_2\,(g) \xrightarrow{hv} 2\,\dot{C}l\,(g)$ (ii)

The chlorine radicals thus formed, initiate the chain reaction for ozone depletion.

Effects of depletion of Ozone Hole

With the depletion of ozone layer, more UV radiation filters into troposphere. UV radiation lead to

(i) Ageing of skin (ii) Cataract

(iii) Sunburn (iv) Skin cancer

(v) Killing of many phytoplankton, damage to fish productivity etc.

Water Pollution

- Pollution of water originates from human activities.
- Easily identified source or place of pollution is called as point source e.g., municipal and industrial discharge pipes where pollutants enter the water- source.
- Non-point sources of pollution are those where a source of pollution cannot be easily identified, e.g., agricultural run off (from farm, animals and crop-lands), acid rain, storm-water drainage (from streets, parking lots and lawns).

Causes of Water Pollution

(i) Pathogens

The most serious water pollutants are the disease-causing agents called pathogens. Pathogens include bacteria and other organisms that enter water from domestic sewage and animal excreta.

(ii) Organic wastes

Organic matter such as leaves, grass, trash etc. pollute water as a consequence of run off.

The large population of bacteria decomposes organic matter present in water. They consume oxygen dissolved in water. In cold water, dissolved oxygen (DO) can reach a concentration up to 10 ppm (parts per million)

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(iii) Chemical Pollutants

Water soluble inorganic chemicals that include heavy metals such as cadmium, mercury, nickel etc. constitute an important class of pollutants.

Biochemical Oxygen Demand (BOD)

- The amount of Oxygen required by bacteria to break down the organic matter present in a certain volume of a sample of water, is called Biochemical Oxygen Demand (BOD).
- The amount of BOD in the water is a measure of the amount of organic material in the water, in terms of how much oxygen will be required to break it down biologically.
- Clean water would have BOD value of less than 5 ppm whereas highly polluted water could have a BOD value of 17 ppm or more.

Eutrophication

The process in which nutrient enriched water bodies support a dense plant population, which kills animal life by depriving it of oxygen and results in subsequent loss of biodiversity is known as Eutrophication.

International Standards for Drinking Water

Fluoride

Fluoride ion concentration deficiency in drinking water causes diseases such as tooth decay etc. Soluble fluoride is often added to drinking water to bring its concentration up to 1 ppm or 1 mg dm^{-3}.

- However, F^- ion concentration above 2 ppm causes brown mottling of teeth. At the same time, excess fluoride (over 10 ppm) causes harmful effect to bones and teeth.
- The F^- ions make the enamel on teeth much harder by converting hydroxyapatite, $[3(Ca_3(PO_4)_2.Ca(OH)_2]$, the enamel on the surface of the teeth, into much harder fluorapatite, $[3(Ca_3(PO_4)_2.CaF_2]$.

Lead

The prescribed upper limit concentration of lead in drinking water is about 50 ppb. Lead can damage kidney, liver, reproductive system etc.

Sulphate

Excessive sulphate (>500 ppm) in drinking water causes laxative effect, otherwise at moderate levels it is harmless.

Nitrate

The maximum limit of nitrate in drinking water is 50 ppm. Excess nitrate in drinking water can cause disease such as methemoglobinemia ('blue baby' syndrome).

Maximum Prescribed Concentration of Some Metals in Drinking Water.

Metal	Maximum Prescribed concentration (ppm or mg dm^{-3})
Fe	0.2
Mn	0.05
Al	0.2
Cu	3.0
Zn	5.0
Cd	0.005

Soil Pollution

Soil pollution as a part of land degradation is caused by the presence of xenobiotic (human-made) chemicals or other alteration in the natural soil environment.

- Open dumps often serve as the breeding ground for rats and flies, rainfall causes leaching of toxic substances.

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Pesticides

Pesticides are basically synthetic toxic chemicals with ecological repercussions. The repeated use of the same or similar pesticides give rise to pests that are resistant to that group of pesticides thus making the pesticides ineffective.

Industrial Waste

(1) Biodegradable Waste

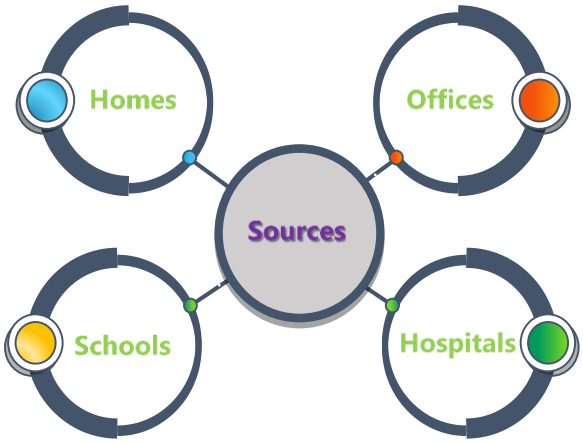
(i) Cotton mills
(ii) Food processing units
(iii) Paper mills
(iv) Textile factories.

(2) Non-Biodegradable Waste

(i) Thermal power plants which produce fly ash.
(ii) Integrated iron and steel plants which produce blast furnace slag and steel melting slag.
(iii) Industries manufacturing Aluminium, zinc and copper produce mud and tailings.
(iv) Fertilizer industries produce gypsum.

Waste Management

Solid waste is not the only waste, which you see in your household garbage box.



Swachh Bharat Mission–Urban (SBM–U)

The SBM–U primarily aims at

- Making Urban India free from open defecation.
- Achieving 100% scientific management of solid waste in the country.

Swachh Bharat Mission–Gramin (SBM–G)

The SBM–G targets to

- Bring about an improvement in the general quality of life in rural areas by promoting cleanliness and hygiene.
- Eliminating open defecation.

Green Chemistry

- Green chemistry is a way of thinking and is about utilising the existing knowledge and principles of chemistry and other sciences to reduce the adverse impact on environment.
- Green chemistry is a production process that would bring about minimum pollution or deterioration to the environment.
- Green chemistry, in a nutshell, is a cost effective approach which involves reduction in material, energy consumption and waste generation.

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Green Chemistry in day-to-day life

(i) Dry Cleaning of Clothes

Tetrachloroethene ($Cl_2C=CCl_2$) was earlier used as solvent for dry cleaning. The compound contaminates the ground water and is also a suspected carcinogen. Replacement of halogenated solvent by liquid CO_2 will result in less harm to ground water.

(ii) Bleaching of Paper

Chlorine gas was used earlier for bleaching paper. These days, hydrogen peroxide (H_2O_2) with suitable catalyst.

(iii) Synthesis of Chemicals

Ethanal (CH_3CHO) is now commercially prepared by one step oxidation of ethene in the presence of ionic catalyst in aqueous medium with a yield of 90%.

$$CH_2=CH_2 + O_2 \xrightarrow{\text{Catalyst}} CH_3CHO\ (90\%)$$

(iv) Green Solution to Clean Turbid Water

Powder of kernel of tamarind seeds has been found to be an effective material to make municipal and industrial waste-water clean. It is non-toxic, biodegradable and cost-effective material. This powder is usually discarded as agricultural waste.

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Purification, Qualitative, Quantitative Analysis

Methods of purification of organic compounds

- Organic compounds obtained either from natural source (or) synthesized in laboratory are contaminated with impurities.
- Various methods are used for removal of impurities from an organic compound depends on the nature of compound and type of impurities present in it.

Note:

Most of the pure compounds contain sharp Melting point and Boiling points.

1. Sublimation

- The process of conversion of sublimable solid to vapour state directly by heating without passing through liquid state is called sublimation.
- This method is used for purification of solids.
- Sublimation process is used for separation of sublimable volatile compounds from non sublimable impurities.
- Sublimation is generally used for purification of camphor, naphthalene, Anthracene, Benzoic acid, phthalic anhydride, Anthraquinone, Indigo, Iodine and solid SO_3.

2. Crystallisation

- Most commonly used technique for purification of solid organic compounds.
- Crystallisation is based on the difference in solubilities of the compound and impurities in a suitable solvent.
- The principle involved in this method is impure compound dissolved in a solvent is sparingly soluble at low temperature, but appreciably soluble at high temperature.
- Insoluble impurities are separated by filtration. The filtrate on cooling saturated solution, pure compound crystallises out.
- If a compound is highly soluble in one solvent and too little soluble in another solvent then crystallisation is carried out by using mixture of these solvents.
- Impurities, which impart colour are removed by adsorbing over activated charcoal.
- Repeated crystallisation is required if organic compound contains impurities of comparable solubilities.

3. Distillation

Distillation is an important method used to separate

(i) Volatile liquids from non-volatile impurities.

(ii) Liquids having sufficient difference in boiling points.

(a) Simple Distillation

- This process is used for purification of liquids which do not undergo decomposition at their boiling points
- The vapourisation of a liquid by heating and subsequent condensation of vapours by cooling is known as distillation.

- Liquid mixture is taken in a round bottom flask and heated carefully, the vapour component with lower boiling point distills first, the vapour formed is condensed by using condenser and the liquid is collected in a receiver. The vapours of component with higher boiling point distills later.
- The liquids that have boiling point difference greater than 40°C can be purified by this method,

Example :
(i) Chloroform (BP. 334 K) and Aniline (B.P. 457 K)
(ii) Ether (B.P. 308 K) and Toluene (B.P. 384 K)
(iii) Benzene (B.P. 353 K) and Aniline (B.P. 457 K)

(b) Fractional Distillation

- Fractional distillation is used if the difference in boiling point of two liquids is less than 40° C.
- Vapours of liquid mixture are passed through fractionating column before condensation, which is fitted over mouth of the round bottom flask.
- Vapours of liquid with higher boiling point condense before the vapours of liquid with lower boiling point.
- The vapours raising up in the fractionating column is richer in more volatile component.
- Each successive condensation and vapourisation unit in the fractionating column is called a theoretical plate.
- Liquids forming a constant boiling mixture (azeotropic mixture) can not be separated by this method.
- Fractional distillation is used to separate different fractions of crude oil in petroleum industry.
- This method is used for separation of mixture of acetone (B.P. 330K) and methyl alcohol (B.P. 338K)

(c) Distillation under reduced pressure (Vacuum Distillation)

- This method is used to purify liquids having very high boiling points, which decompose at or below their boiling points.
- These liquids are made to boil at a temperature lower than their normal boiling point by reducing pressure on their surface with the help of vacuum pump.
- Glycerol can be separated from spent-lye in soap industry by using vacuum distillation.

(d) Steam Distillation

- This method is used for separation and purification of organic compounds (solids or liquids) which are steam volatile and are insoluble in water.
- In steam distillation, steam from a steam generator is passed through a heated flask containing the liquid to be distilled. The mixture of steam and the volatile organic compound is condensed and collected. The compound is later separated from water using a separating funnel.
- In steam distillation, the liquid boils when the sum of vapour pressures due to the organic liquid (p_1) and that due to water (p_2) becomes equal to the atmospheric pressure (p), i.e. $p = p_1 + p_2$. Since p_1 is lower than p, the organic liquid vaporises at lower temperature than its boiling point.
- Compounds which can be purified by steam distillation are aniline, nitrobenzene, o-nitrophenol.

4. Solvent Extraction (Differential Extraction)

- If an organic compound in aqueous medium is separated by mixing it in organic solvent in which it is more soluble than in water.
- Organic solvent should be immiscible with water.
- Organic solvent and aqueous solution are immiscible with each other, so they can form two distinct layers (which can be separated by separatory funnel).
- If organic compound is less soluble in organic solvent then large quantity of solvent is required to extract small quantity of compound, which is said to be continuous extraction.
- Benzoic acid can be extracted from its aqueous solution using benzene as solvent.

5. Chromatography

- This method is used for separation of mixtures into their components.
- Chromatography is obtained from the greek word "Chroma" means colour.
- This method was first used for separation of coloured substances found in plants.
- This technique have two phases
  (i) Stationary phase: The mixture of substance is applied on this phase.
  (ii) Mobile phase: A solvent or gas is allowed to move slowly over the stationary phase
- The component of mixture gets gradually separated from one another.
- Based on the principle involved chromatography is classified in to
  (a) Adsorption Chromatography and (b) Partition Chromatography

(a) Adsorption Chromatography

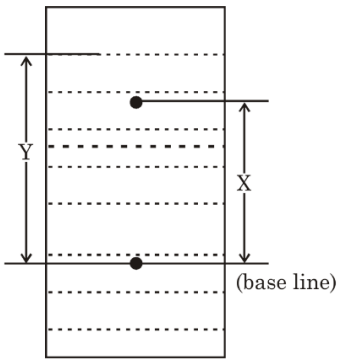
- Adsorption chromatography is based on the fact that different compounds are adsorbed on an adsorbent to different degrees.
- Commonly used adsorbents are silica gel, alumina.
- Adsorption chromatography is of two types
  (i) Column chromatography; (ii) Thin layer chromatography (TLC)

(i) Column Chromatography

- The mixture to be separated (adsorbent) is placed at the top of the stationary phase.
- An appropriate eluent (solvent) is allowed to flow down the column slowly.
- The strongly adsorbed substances are retained near the top and others come down to various distances in the column.

(ii) Thin Layer Chromatography (TLC)

- A glass plate is coated with adsorbent (ex: silica gel, alumina) as a thin layer (about 0.2mm thick) is called chromatography plate or chroma plate.
- The solution of mixture to be separated is applied as small spot about 2cm above from one end of the TLC plate.
- The glass plate is placed in a closed jar containing the eluent. As the eluent rises up, the components of the mixture move up along the eluent to different distances depending on their degree of adsorption and separation takes place.
- The relative adsorption of each component of the mixture is expressed in terms of its retardation factor i.e, Rf value.



$$R_f = \frac{\text{Distance moved by the substance from base line (x)}}{\text{Distance moved by the solvent from base line (y)}}$$

- The spots of coloured compounds are visible on TLC plate due to their original colour.
- The colourless compound which fluoresce are detected with ultraviolet light.
- Amino acids are detected by spraying the plate with ninhydrin solution.

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(b) Partition Chromatography

- Partition chromatography is based on continuous differential partitioning of components of a mixture between stationary and mobile phases.
- Paper chromatography is a type of partition chromatography.
- A special quality paper known as chromatography paper, is used.
- Chromatography paper contains water (as a stationary phase).
- At the base of jar a suitable solvent act as mobile phase.
- The solvent rises up the paper by capillary action and flows over the spot.
- The paper selectively retains different component according to their differing partition in the two phases. The paper strip so developed is called chromatogram.
- The spots of the separated coloured compounds are visible at different heights from the position of initial spot on the chromatogram.
- The spots of the separated colourless compound may be observed either under ultraviolet or by the use of appropriate spraying agent.

Qualitative Analysis of Organic Compounds (Detection of elements)

- The qualitative analysis of an organic compound involves detection of all elements present in it.

Detection of Carbon and Hydrogen

- Carbon and hydrogen are detected by heating the compound with cupric oxide (CuO).
- Carbon present in the compound is oxidised to carbondioxide, which turns lime water milky.

$$C + 2CuO \xrightarrow{\Delta} 2Cu + CO_2$$

$$CO_2 + Ca(OH)_2 \longrightarrow CaCO_3 + H_2O$$

- Hydrogen present in the compound is converted into water, which turns anhydrous copper sulphate into blue.

$$H_2 + CuO \xrightarrow{\Delta} Cu + H_2O$$

$$CuSO_4 + 5H_2O \longrightarrow CuSO_4 \cdot 5H_2O$$

Anhydrous (Colourless) **Hydrated (Blue)**

Detection of Nitrogen, Sulphur Halogens and Phosphorus

- Nitrogen, sulphur, halogens and phosphorus present in an organic compound are detected by Lassaigne's test.
- Organic compounds are fused with dry sodium in fusion tube and Na fusion extract is obtained.
- The following reactions takes place

$$Na + C + N \xrightarrow{\Delta} NaCN$$

$$2Na + S \xrightarrow{\Delta} Na_2S$$

$$2Na + X_2 \xrightarrow{\Delta} 2NaX \quad \textbf{(X=Cl, Br or I)}$$

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(1) Test for Nitrogen

- Sodium fusion extract is boiled with freshly prepared ferrous sulphate ($FeSO_4$) solution and then acidified with concentrated sulphuric acid. The formation of Prussian blue colour confirms the presence of nitrogen.

$6NaCN + FeSO_4 \longrightarrow Na_4[Fe(CN)_6]_3 + Na_2SO_4$

$FeSO_4 + H_2SO_4 \longrightarrow 2Fe_2(SO_4)_3$

$3Na_4[Fe(CN)_6] + 2Fe_2(SO_4)_3 \longrightarrow Fe_4[Fe(CN_6)_3 + 6Na_2SO_4$

Ferriferrocyanide

(Prussian Blue)

- This test fails in case of diazo compounds. **(—N≡N—)**

(2) Test for Sulphur

(i) Sodium fusion extract is reacted with lead acetate, a black precipitate of lead sulphide is formed, which indicates presence of sulphur.

$Na_2S + (CH_3COO)_2Pb \longrightarrow PbS\downarrow + 2CH_3COONa$

Black

(ii) Sodium fusion extract is treated with freshly prepared sodium nitroprusside, appearance of violet colour (purple) indicates presence of sulphur.

$Na_2S + Na_2[Fe(CN)_5NO] \longrightarrow Na_4[Fe(CN)_5NOS]$

(Sodium Nitro Prusside) **(Violet)**

- In case both nitrogen and sulphur are present in an organic compound sodium thiocyanate is formed, which gives blood red colour with Fe^{+3}.

$Na + C + N + S \longrightarrow NaCNS$ **(Sodium fusion)**

$Fe^{+3} + SCN^- \longrightarrow [Fe(SCN)]^{+2}$ **(No Prussian blue means no free CN^-)**

(Blood red)

- If sodium fusion is carried out with excess of sodium, the thiocyanate decomposes to yield cyanide and sulphide, these ions gives their usual tests.

$NaSCN + 2Na \longrightarrow NaCN + Na_2S$

(3) Test for Halogens

- Sodium fusion extract is acidified with nitric acid and then treated with silver nitrate solution.
- White precipitate, soluble in ammonium hydroxide indicates presence of chlorine.

$NaCl + AgNO_3 \longrightarrow AgCl\downarrow + NaNO_3$

(White ppt)

$AgCl + 2NH_4OH \longrightarrow [Ag(NH_3)_2Cl] + 2H_2O$

(Soluble complex)

$NaBr + AgNO_3 \longrightarrow AgBr\downarrow + NaNO_3$

(Yellow ppt)

(Sparingly Soluble in NH_4–OH)

$NaI + AgNO_3 \longrightarrow AgI\downarrow + NaNO_3$

(Yellow precipitate)

(Insoluble in NH_4OH)

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(4) Test for Phosphorus

- The compound is heated with oxidising agent (sodium peroxide) phosphorus present in the compound is oxidised to sodium phosphate.
- The solution is boiled with nitric acid and then treated with ammonium molybdate, a canary yellow (ammonium phospho molybdate) precipitate formation indicates presence of phosphorus.

$$2P + 5Na_2O_2 \xrightarrow{\Delta} 2Na_3PO_4 + 2Na_2O$$

$$Na_3PO_4 + 3HNO_3 \longrightarrow H_3PO_4 + 3NaNO_3$$

$$H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 \longrightarrow (NH_4)_3PO_4 \cdot 12MoO_3 + 21NH_4NO_3 + 12H_2O$$

Quantitative Analysis

Estimation of Carbon and Hydrogen

- CO_2 and H_2O produced are weighed by absorbing in concentrated solution of potassium hydroxide and anhydrous calcium chloride (or) magnesium perchlorate respectively

$$\%C = \frac{12}{44} \times \frac{\text{Weight of } CO_2 \text{ formed}}{\text{Weight of organic compound}} \times 100$$

$$\%H = \frac{2}{18} \times \frac{\text{Weight of } CO_2 \text{ formed}}{\text{Weight of organic compound}} \times 100$$

Estimation of Nitrogen

- Nitrogen present in organic compound is estimated by
  (1) Dumas Method, (2) Kjeldahl's Method

(1) Dumas Method

- In this method nitrogen present in the organic compound is converted in to N_2 (molecular nitrogen)
- A weighed amount of organic compound is heated with cupric oxide in an atmosphere of carbondioxide.
- Carbon and hydrogen present in the compound are oxidised to CO_2 and H_2O, while N_2 is free.

$$C_xH_yN_z + \left(2x + \frac{y}{2}\right)CuO \longrightarrow xCO_2 + \frac{y}{2}H_2O + \frac{z}{2}N_2 + \left(2x + \frac{y}{2}\right)Cu$$

- Some oxides of nitrogen formed are reduced to free nitrogen by passing over heated copper gauze
- The mixture of gases produced is collected over caustic potash solution (KOH solution) which absorbs CO_2.
- Nitrogen is collected in the upper part of nitro meter.
- Now volume of nitrogen is calculated at STP.

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

V_1 = Volume of N_2 gas

P_1 = Pressure of N_2 – Aqueous tension

T_1 = Room temperature

$$V_2 = \frac{P_1V_1 \times 273}{T_1 \times 760}$$

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- Calculations of % nitrogen

  ∵ 22400 ml of N_2 at STP weight = 28gm

  $\therefore$ V ml of N_2 at STP weight = $\frac{28}{22400} \times V$ gm

  $\%N_2 = \frac{28}{22400} \times \frac{V}{W} \times 100$; W = Weight of organic substance

(2) Kjeldahl's Method

- In this method nitrogen in the organic compound is converted into ammonia (NH_3)
- A known mass of organic compound containing nitrogen is heated with concentrated sulphuric acid in presence of K_2SO_4 and $CuSO_4$ then nitrogen present in the compound is converted into ammonium sulphate. K_2SO_4 increases boiling point of H_2SO_4 and $CuSO_4$ acts as catalyst.
- Organic compound + $H_2SO_4 \longrightarrow (NH_4)_2SO_4$
- The resulting solution is distilled with excess of sodium hydroxide

  $(NH_4)_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2NH_3 + 2H_2O$
- Ammonia gas is absorbed in excess of standard solution of H_2SO_4.

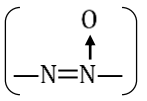
  $NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$
- The amount of ammonia produced is determined by estimating the amount of H_2SO_4 consumed.

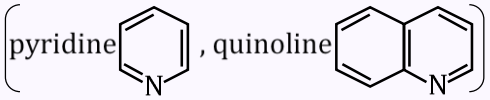
  Normality of H_2SO_4 taken = N_1
  Volume of H_2SO_4 taken = V_1
- Estimation of H_2SO_4 is done by titrating the H_2SO_4 left after absorption of ammonia with standard alkali solution.

  Normality of NaOH taken = N_2
  Volume of NaOH taken = V_2
- The difference between the initial amount of acid taken and that left after absorption of ammonia is the amount of H_2SO_4 used.
- ∵ Milli equivalent of H_2SO_4 used for neutralization of Produced NH_3
  = Milli equivalent of NH_3
  = $(N_1V_1 - N_2V_2)$
- ∵ 1000 ml of 1N NH_3 contain 14 gm Nitrogen

  ∵ $(N_1V_1 - N_2V_2)$ ml of 1N NH_3 contain = $\frac{14}{1000} \times (N_1V_1 - N_2V_2)$ gm N_2

  Then % of N = $\frac{14}{1000} \times \frac{N_1V_1 - N_2V_2}{W} \times 100$

  Then % of N = $\frac{1.4}{W} \times (N_1V_1 - N_2V_2)$; mass of organic substance is W g.
- This method is not applicable to compounds containing nitro ($-NO_2$), Nitroso (NO), azo group ($-N=N-$), azoxy compounds  and nitrogen present in the ring

  because nitrogen present in these compounds is not quantitatively converted into ammonium sulphate.

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Estimation of Halogens (Carius Method)

- A weighed amount of an organic compound is heated with fuming nitric acid in the presence of silver nitrate contained in a hard glass tube known as Carius tube.
- Carbon and hydrogen present in the compound is converted into CO_2 and H_2O.
- Halogen present in the organic compound is converted into silver halide.
- The precipitate is washed, dried and weighed

$$\text{Percentage of halogen} = \frac{\text{atomic weight of halogen}}{\text{Mol weight of silver halide}} \times \frac{\text{Weight of silver halide formed}}{\text{weight of organic compound}} \times 100$$

$$\%\ \text{Cl} = \frac{35.5}{143.5} \times \frac{\text{Weight of AgCl formed}}{\text{weight of organic compound}} \times 100$$

$$\%\ \text{Br} = \frac{80}{188} \times \frac{\text{Weight of AgBr formed}}{\text{weight of organic compound}} \times 100$$

$$\%\ \text{I} = \frac{127}{235} \times \frac{\text{Weight of AgI formed}}{\text{weight of organic compound}} \times 100$$

Estimation of Sulphur

- A weighed amount of organic compound is heated in a Carius tube with sodium peroxide or fuming nitric acid.
- Sulphur present in the compound is oxidised into sulphuric acid, which is treated with $BaCl_2$ solution and gives precipitate of $BaSO_4$.
- It is filtered, the precipitate is washed, dried and weighed.

$$\%\ \text{S} = \frac{\text{Atomic weight of Sulphur}}{\text{Mol. weight of } BaSO_4} \times \frac{\text{Weight of } BaSO_4 \text{ formed}}{\text{weight of organic compound}} \times 100$$

$$\%\ \text{S} = \frac{32}{233} \times \frac{\text{Weight of } BaSO_4 \text{ formed}}{\text{weight of organic compound}} \times 100$$

Estimation of Phosphorus

- A weighed amount of organic compound is heated with fuming nitric acid, then phosphorus present in the compound is oxidised to phosphoric acid. Phosphoric acid is precipitated as magnesium ammonium phosphate (NH_4MgPO_4), by addition of magnesia mixture ($MgCl_2 + NH_4OH + NH_4Cl$).
- Magnesium ammonium phosphate is washed, dried and it is heated strongly to get magnesium pyrophosphate ($Mg_2P_2O_7$).

$$H_3PO_4 \xrightarrow{\text{Magnesia mixture}} MgNH_4PO_4$$

(Phosphoric acid) (Magnisium ammonium phosphate)

$$2MgNH_4PO_4 \xrightarrow{\Delta} Mg_2P_2O_7 + 2NH_3 + H_2O$$

(Magnesium pyrophosphate)

$$\%\ \text{P} = \frac{62}{222} \times \frac{\text{Weight of } Mg_2P_2O_7 \text{ formed}}{\text{weight of organic compounds}} \times 100$$

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BEGINNER'S BOX-2

1. 0.3960 gm of an organic compound on combustion gives 0.792 gm CO_2 and 0.324 gm of H_2O. Calculate the % of C and H
(1) 54.55% and 9.09% (2) 9.09% and 54.55%
(3) 35% and 65% (4) 65% and 35%

2. 0.25 gm of an organic compound at NTP gives 31 ml of N_2 gas by Duma's method. Find out of % of N
(1) 14.5 (2) 15.5 (3) 16.5 (4) 20.5

3. 31.7 ml of moist N_2 was obtained from 0.2033 gm of an organic compound in Duma's method at 14°C and 758 mm pressure. If aq. tension at 14°C = 14 mm than calculate % of N
(1) 15% (2) 18% (3) 25% (4) 30%

4. 30 ml 0.25 N H_2SO_4 are used in neutralizing NH_3 obtained from 0.75 gm of an organic compound in Kjeldhal's method find out % of N in the compound
(1) 7% (2) 14% (3) 21% (4) 28%

5. In Kjeldhal's method, NH_3 evolved from 0.25 gm of an organic compound was passed into 30 ml N/2 H_2SO_4. 50 ml N/10 NaOH were required to neutralize the unreact acid, calculate % of N.
(1) 14% (2) 28% (3) 42% (4) 56%

6. 0.35 gm of an organic compound was analysed by Kjeldhal's method. Ammonia evolved was absorbed in 100 mℓ $\frac{N}{10}$ H_2SO_4. Unused acid required 30 mℓ $\frac{N}{10}$ NaOH for neutralisation calculate % of N
(1) 28% (2) 14% (3) 56% (4) 42%

7. In Duma's method estimation of nitrogen, 0.3g of an organic compound gave 50 ml of nitrogen collected at 300 K temperature and 715 mm pressure. Calculate the percentage composition of nitrogen in the compound. (Aqueous tension at 300K = 15 mm)
(1) 10.46% (2) 17.46% (3) 27.46% (4) 35.46%

8 During estimation of nirtogen present in an organic compound by Kjeldahl's method, the ammonia evolved from 0.5 g of the compound in Kjeldahl's estimation of nitrogen, neutralized 10 mℓ of 1 M H_2SO_4. Find out the percentage of nitrogen in the compound.
(1) 24% (2) 42% (3) 56% (4) 28%

9. In carius method of estimation of halogen, 0.15g of an organic compound gave 0.12 g of AgBr. Find out the percentage of bromine in the compound.
(1) 34% (2) 51% (3) 17% (4) 25%

10. In sulphur estimation, 0.157g of an organic compound gave 0.4813 g of barium sulphate. What is the percentage of sulphur in the compound ?
(1) 21.1% (2) 52.1% (3) 42.1% (4) 31.1%

BEGINNER'S BOX — ANSWERS KEY

BEGINNER'S BOX-1	Que.	1	2	3	4	5
	Ans.	1	3	3	4	2

BEGINNER'S BOX-2	Que.	1	2	3	4	5	6	7	8	9	10
	Ans.	1	2	2	2	4	1	2	3	1	3